

## LABELING WITH POLYMERIC LABELS HAVING AN ACTIVATED HYDROPHILIC LAYER

## FIELD OF THE INVENTION

- 10 This invention relates to polymeric sheets or rolls particularly adapted for use as labels in the post mold labeling of plastic, glass or metal containers or surfaces. More particularly, the present invention relates to polymeric film substrates adapted for printing
- 15 that also have a hydrophilic surface layer activatable into an adhesive layer for use as labels in post mold labeling applications using conventional wet applied water based labeling equipment typically used for the application of paper labels. In another aspect the
- 20 invention relates to such labels which possess the beneficial properties of the known plastic label substrates, but which are able to be applied on conventional post mold paper labeling equipment using wet applied water based solutions comprising water, water
- 25 blended with a selected cross-linking agent, adhesives or adhesives blended with a selected cross-linking agent.

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## BACKGROUND OF THE INVENTION

Plastic and glass containers or bottles are prevalent in a wide variety of shapes and sizes for holding many different types of materials such as detergents, chemicals, motor oil, beer, etc. These containers are glass or plastic (mono or multi layers) of polyethylene, polypropylene, polyester or vinyl along with other specialty blends for specific barrier and product resistance performance. Generally such containers are provided with a label which designates the trade name of the product and may contain other information as well. The early art which still is prevalent today employed the use of labels manufactured from paper substrates that were applied with a water based adhesive. Subsequently, dry pressure sensitive self adhesives and in mold labels manufactured from paper have been and continue to be used. The shortcomings of paper labels with regard to tearing, wrinkling, creasing and the like due to age and moisture, or due to a lack of deformability when applied to a deformable plastic substrate have been well documented in the labeling industry. Because of this and the need to produce recyclable plastic containers, over the years a great deal of effort has been expended to develop container decoration techniques and durable film substrates which would overcome these shortcomings.

Polymeric film facestocks for container decoration which have resulted from these efforts can be applied to glass and plastic containers as self adhesive pressure sensitive labels as described in the prior art. The use of self adhesive paper and film "pressure sensitive adhesive" (PSA) labels that have been preprinted and

- 5 supported on a release liner is not a cost effective  
option because of the added cost of the release liner  
used to support and render processable the self adhesive  
face stock. The cost of this type of structure combined  
with the added cost of disposal of the liner does not  
10 make pressure sensitive labeling a desirable option from  
an economic or environmental standpoint for high volume  
applications. In addition, PSA labelers typically run  
much slower than cold glue labelers and capital  
investment in new labeling equipment is required to  
15 transition from wet applied Post Mold Labels (PML) to  
self adhesive PSA labels. Also a factor is the effect of  
a new process on an existing packaging line in terms of  
learning curve and experience.
- 20 Another film face stock labeling technique that has  
evolved is the use of heat activated in-mold labels as  
described in the prior art where a preprinted plastic  
label with a heat activated adhesive is placed in the  
mold before the molten plastic resin is injected or blown  
25 into the mold cavity at elevated temperature and pressure  
which activates the adhesive and fuses the label  
substrate to the container in-mold resulting in a pre-  
decorated container as it exits the mold.
- 30 The use of polymeric film based in-mold label substrates  
presents a more cost effective alternative than self  
adhesive pressure sensitive labels in terms of substrate  
cost but as this technology has progressed, it has been  
found that productivity is impacted by the label feeding  
35 step into the mold which is performed in a complex,  
continuous and rapid manner which results in large  
amounts of scrap material. Also, the initial capital

5 investment required to tool up for a container specific  
in-mold label process for new molds and the complex  
electromechanical maintenance intensive feeding devices  
is significant. Another detriment for this process is the  
potential inventory carrying costs for varieties of  
10 labeled containers that come into play with predecorated  
containers such as in-mold for those who would choose to  
apply the label immediately pre or post filled.

Post mold decoration of glass and plastic containers in  
15 the current art can also be accomplished by direct screen  
printing on the container. Direct screen printing on the  
container is not a cost effective process and also  
presents the aforementioned inventory problems along with  
added cost for freight to and from a screen printer. The  
20 graphical possibilities for label copy are limited in  
terms of cost and quality with this technique. Commodity  
products can not support the cost of this labeling  
technique.

25 Another post mold technique that has been popular is the  
"Therimage" process. This process transfers a reverse  
printed image from a transfer release sheet under  
temperature and pressure to produce decorated containers.  
The "Therimage" technique of transferring a reverse  
30 printed image is costly because of transfer sheet costs  
and presents the same disposal problems and costs with  
the transfer sheet as occurs with the aforementioned  
release liner used in conjunction with self adhesive  
labels. Graphic design and quality is limited with this  
35 technique.

Other techniques for labeling various plastic and glass  
containers with preprinted paper or film label substrates

5 include the use of hot melt adhesives (not aqueous) which  
are applied to the label substrate or container in a  
molten state with container and substrate subsequently  
married while the hot melt is molten. When the hot melt  
adhesive cools, it sets up and bonds the label substrate  
10 to the container. This technology requires the use of  
sophisticated melting and application equipment that must  
be operated, cleaned and maintained at elevated  
temperatures. This technology works well with complete  
360 degree wrap around labels but has not evolved to the  
15 point to allow consistent labeling of a die cut or square  
cut label with less than 360 degree wrap. Affixing a cut  
label to an area on a container with 100% or patterned  
adhesive application using hot melt adhesives has not  
been commercially perfected. Complete wrap around hot  
20 melt applied labels where one end of the label is affixed  
to the container while the other end is wrapped around  
the container and affixed with hot melt to the label  
substrate is proven hot melt label application technology  
that works well for film and paper label substrates. This  
25 technology does not fit for individually labeled panels  
on a container such a rectangular oil, contoured  
detergent or beer containers where discrete labels are  
applied such as a neck label, front label or rear label  
that are not wrapped around 360 degrees. Another drawback  
30 is the added cost for label substrate when this technique  
is used since more label substrate is required because of  
the 100% wrap around.

Lastly, one of the oldest and still prevalent labeling  
35 techniques is the application of paper based labels to  
glass and plastic containers using natural and synthetic  
labeling adhesives such as BL300 produced by Henkel  
Adhesives or OC363-20 produced by O.C. Adhesives Corp.

5 which are known in the art. This is a safe (water based)  
proven technology that has grown and been employed for  
many years and consequently there are many existing  
machines that have been installed for this type of  
labeling technique such as from Krones, Neutraubling,  
10 Germany that run cut precut labels or Koyo, Japan which  
runs roll stock that is cut on machine to the label size.  
The cut label techniques and associated adhesives work  
well with paper based substrates applied to glass,  
plastic or metal containers because the wet adhesive  
15 wicks (absorbs) into the paper substrate from the  
applicator roll, pad or pallet which breathes and allows  
the moisture from the water carrier to be absorbed by and  
dry thru the paper base.

20 This technique obviously will not work well with non-  
porous polymeric substrates as the adhesive can not wick  
into the polymeric substrate for initial tack and  
adhesive transfer to the label or drying thru the  
plastic. Typically, wet applied cut label machines work  
25 where glued pallets rotate and come in contact with a  
glue applicator roll and become wetted with adhesive. The  
adhesive wetted pallet then is pressed in contact with  
the back side of the paper label where the adhesive  
penetrates the paper fiber with enough initial tack to  
30 remove the label out of the label holding magazine while  
simultaneously gluing the back side of the label. This is  
accomplished by applying a thin glue film to the pallet  
picked up from the applicator roll metering system in a  
pattern or with 100% coverage which is then pressed in  
35 intimate contact against the first label in the stack.  
The glue roller and pallet systems in the current art  
typically employ a steel glue roller and a hard rubber  
pallet with a durometer greater than 60 or a rubber glue

5 roller and an aluminum or coater steel pallet. Either combination provides for a firm pallet to transfer the adhesive.

10 After its removal, the label sticks on the entire glued area of the pallet until transferred to a "gripper" cylinder and removed from the pallet typically using a vacuum mechanism. The gripper cylinder then transfers the label to the container to be labeled. The various machine designs and techniques are well known within the labeling  
15 industry and to those skilled in the art. The "Krones Manual Of Labeling Technology" by Hermann Kronseder dated December 1978, is hereby incorporated by reference.

In recent years, as described in U.S. 6,663,746 and 6,517,664, which are incorporated by reference, polymeric  
20 film labels using a hydrophilic glue receptive layer and a water based adhesive composition are now being used. The applications also describe the concept of rewetting the hydrophilic layer with an aqueous medium (water or adhesive that may contain a cross-linking agent) to  
25 activate the hydrophilic layer into an adhesive layer.

Attempts have been made to use polymeric substrates with high moisture vapor transmission rates (MVTR) and tacky or pressure sensitive adhesive on conventional labeling equipment with little success. The tacky adhesive  
30 required to stick to the water impervious polymeric substrate causes machining problems by gumming up the adhesive application system and creates cleanup issues. The high MVTR substrates also did not have good wet tack with existing commercially available adhesives that would  
35 machine without problems and did not dry rapidly enough making the labels prone to "swimming" or moving from the desired application area during down stream processing.

5 In addition, the adhesives do not wet out and apply  
uniformly to non hydrophilic surfaces with the crude  
adhesive metering and application systems currently in  
use on existing paper labeling machinery. Without uniform  
application, wet out and wet tack, it will be impossible  
10 to apply a clear label that has the no label look because  
of adhesive and application imperfections. Recent  
developments in radiation curable (not aqueous) adhesives  
adapted for use on cut and stack labelers referenced in  
issued and pending patent applications to McNutt et. al.  
15 have led to the development of more sophisticated  
adhesive metering mechanisms and label wipers and  
techniques that can be used to uniformly control adhesive  
deposition and these modifications are contemplated for  
use to apply the aqueous activation medium to the  
20 activatable layer of the current invention at the minimum  
possible level.

The techniques of U.S. 6,517,664 and U.S. 6,663,746 which  
are now being performed commercially and those developed  
by McNutt et al use adhesives applied to the polymeric  
25 film on the labeling machine to affix the label to the  
container and work well for opaque labels. There are  
still inconsistencies and imperfections in the  
application of the adhesive such as bubbles and heavy or  
light adhesive areas that when applied to clear or  
30 contact clear substrates appear inferior when compared to  
PSA labels where the adhesive has been pre-coated on the  
substrate. In addition, the radiation curable adhesives  
as defined by McNutt et. al. are very costly when  
compared to aqueous systems and in comparison are health  
35 and environmental unfriendly.

Accordingly, it is an object of the invention to provide



- 5 a polymeric label particularly adapted for use in post  
mold wet applied labeling of polymeric, glass and metal  
containers that has a dry non pressure sensitive  
hydrophilic layer uniformly pre-applied that can be  
activated into a defect free adhesive layer. This is  
10 accomplished by pre-applying by coating, coextrusion or  
extrusion the layer that is activated on the labeling  
machine with an aqueous medium to become tacky and  
function as an adhesive to affix the polymeric label to  
the container. The activated label will readily feed from  
15 the label magazine or gripper, adhere with sufficient  
tack without moving through post labeling handling and  
processing including but not limited to conveying,  
filling, case packing and palletizing.
- 20 It is a primary object of the invention to provide a  
polymeric label with a pre-applied hydrophilic layer  
consisting of at least 30% dry by weight of animal glue  
activated into an adhesive layer through an aqueous  
medium on the labeler particularly adapted for use in  
25 post mold wet applied labeling of polymeric and glass  
containers that would have sufficient wet tack and  
affinity for water, a water based solution or adhesive  
used to allow for transfer of the water, water based  
solution or water based adhesive to the polymeric label  
30 substrate from the applicator roll(s), pad(s) or  
pallet(s) of the labeling machine to activate it into an  
adhesive.

It is also an object of the invention to provide an  
35 activatable polymeric label for use in post mold wet  
applied labeling of polymeric and glass containers that  
would have a coefficient of expansion or contraction  
under the conditions which the container sees which is

- 5 the same or compatible with that of the polymeric resin, glass or metal from which the container is made so that expansion and contraction of the container will not wrinkle or otherwise affect the integrity of the label.
- 10 It is also an object of the invention to provide a polymeric label for use in wet applied post mold labeling which would combine suitable properties of modulus of elasticity and flexibility and would not be degraded by handling and flexing of the subsequent container.
- 15 Finally, it would be desirable to provide a label for use in wet applied post mold labeling of polymeric containers which does not have to be removed from such containers in order to recycle or regrind defective or post consumer polymeric containers.

20 SUMMARY OF THE INVENTION

In considering the performance or economic shortcomings of prior art materials, I have discovered an improvement to the process as described in the pending and issued applications by the applicant as cited above by which a

25 polymeric label with a uniform pre-applied hydrophilic layer comprising at least 30% by dry weight of a animal glue can be applied to a container by activating the hydrophilic layer to form a tacky adhesive when wet on

30 the labeler by an aqueous medium before being applied to a glass, plastic or metal container or surface. The process may be carried out in a more consistent and uniform manner than a labeling process that uses a non activatable layer that requires a heavy adhesive layer

35 applied on the label machine to function. The method of the invention comprises:

- 5 (a) applying a uniform layer of a hydrophilic solid material containing at least 30% by dry weight of animal glue to a polymeric label based on the combined weight of the hydrophilic solid material and the weight of the animal glue and any additive, e.g. cross-linker, and optionally drying said hydrophilic solid material to form an activatable hydrophilic layer on said polymeric label that can be activated into a tacky adhesive; (b) applying a light deposition water, water containing a cross-linking agent, a water based adhesive or a water based adhesive containing a cross-linking agent over said activatable hydrophilic layer to form a tacky fastenable polymeric label free of bubbles and uneven adhesive streaks typical of the standard deposition of adhesives applied on aqueous labelers;
- 10
- 15
- 20 (c) fastening said fastenable polymeric label to a glass, plastic or metal container or surface; and
- (d) curing said polymeric label on said glass, plastic or metal surface or container.
- 25

Containers labeled according to the process of the invention, where a cross-linker is present in the dried adhesive composition, are novel articles as they have a label that has not been previously described.

30

For opaque or metalized labels, special mention is made that it is preferable to use a coextruded polymeric label substrate with a cavitated or voided adhesive surface producing micro-voids or pores on the adhesive side in combination with a porous core. Typically these types of label substrates have a density  $<0.9$  where the adhesive penetrates the rear plane of the label wherein said

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5 polymer label contains a portion of said dried water based adhesive within said micro-voided or cavitated polymer label. These label substrates have a density <0.9, preferably below 0.55 to 0.85 and more preferably, from 0.6 to 0.75, and are made of polymers such as  
10 polyethylene, polypropylene, polyester, i.e. polyethylene terephthalate, polystyrene, polycarbonate, vinyl, cellophane or compatibilized polymer blends which are described in U.S. 6,517,664, which is incorporated by reference.

15 The use of the low density micro-voided polymer film can allow portions of the water based adhesive to migrate into the film during the drying cycle to provide an enhanced bond between the polymeric label and the  
20 container surface and to also impart stiffness to the dried label on the container surface. Additionally, the weak internal strength of the voided material provides the appearance of superior bond when it is attempted to remove the label because it fractures apart at minimal  
25 force. Additionally, the pores create greater surface area for bonding versus a polymeric film with a smooth adhesive surface.

Most importantly, it has been found that voided substrates with a porous adhesive side that are  
30 judiciously applied with a hydrophilic layer on the adhesive side show superior adhesion when rewet and pressed onto the glass metal or plastic container because the voided area or open area of the pore has a greater surface area than a non voided smooth surface and appears  
35 to act as a suction cup when the air in the cavitated or voided area is pressed out as the label is applied providing an improved bond while pulling activating aqueous medium into the pores.

## 5 DETAILED DESCRIPTION OF THE INVENTION

Pre-applied activatable hydrophilic materials containing animal glue that can function as an adhesive are formulated so that their coefficients of expansion or contraction, thickness and modulus of elasticity when applied to a polymer film will result in a polymeric film facestock that will have hydrophilicity, absorbtivity, wet tack and drying properties that will permit the polymer film to be applied to polymeric, glass or metal containers via water based wet labeling techniques on standard paper labeling equipment.

It is contemplated that the pre-applied hydrophilic material will be dried on the polymeric substrate and rewetted at the time that the labeling material is applied to a container. It is also contemplated that the hydrophilic material may be applied at the time of labeling a container just prior to the time when the label is directly applied to a container without drying the hydrophilic material and rewetting the hydrophilic material at the time of labeling. The apparatus which is used to apply paper labels is well known to those in the art. The polymeric label substrate with the activatable hydrophilic layer will demonstrate sufficient "wet tack" during the label application period and the label drying period to permit containers to be handled and processed. The polymeric film based facestock will provide a label with printability, chemical and dimensional stability, resistance to cracking, tearing, creasing, wrinkling or any other degradation of the sort experienced by paper labels due to physical or environmental extremes.

The invention also permits the use of hydrophilic layer activatable by a water based solution into an adhesive to be used to fasten a clear or contact clear polymeric film substrate which is reverse printed and then over coated with the activatable hydrophilic layer to a

- 5 container. As used herein the reference to a "container" includes a surface of an object made of glass, plastic or metals such as bottles, cans, toys and building materials.
- 10 The activatable hydrophilic component or blends containing animal glue will be applied in the present invention to the selected polymeric sheet in a continuous or patterned layer to provide the absorptive, wet tack and drying properties that are necessary to enable
- 15 polymeric sheets to be successfully used as label substrates on polymeric or glass containers when activated through wetting with water, water and a cross-linker, adhesive or adhesive and a cross-linker using water based wet labeling techniques where the apparatus
- 20 is configured to apply the minimum amount of aqueous solution to activate the layer into a tacky adhesive when wet, but not excess aqueous medium to saturate the activatable layer causing it to loose its adhesive properties and not adhere well and take a long time to
- 25 dry. The activatable hydrophilic layer, containing at least 30% by weight of animal glue based on the weight of the hydrophilic solid material and the animal glue which may be applied by either a coating, coextrusion or an extrusion technique, has the function of absorbing
- 30 moisture to activate the layer as an adhesive when wet with an aqueous medium thus causing selected hydrophilic layers to function as an adhesive without any applied adhesive as is conventionally performed on aqueous labeling machines in the art or to activate by absorbing
- 35 the moisture from an aqueous adhesive if used, to cause the polymer film to adhere to the glass, plastic or metal container and to set up rapidly and positively. It is important or key to this invention to minimize the amount of aqueous medium used to activate the hydrophilic layer
- 40 as an adhesive. Excess activation moisture decreases the tack of the activated layer as it becomes saturated with moisture and will lead to longer drying times and loss of

5 adhesion properties. Additionally, the ability to  
minimize machine applied imperfections such as bubbles  
and streaks typical as previously mentioned in the  
current art when heavy adhesive layers are applied on the  
labeling machine is dictated by the amount of activating  
10 medium used and if excess is used, it detracts from the  
concept of a pre-applied defect free adhesively activated  
hydrophilic layer.

It is also possible to coextrude the activatable  
15 hydrophilic layer with the polymer film layer.

The choice of polymeric substrate for the label film will  
determine the rigidity, deformability or conformability,  
regrindability, printability and expansion or contraction  
20 characteristics required for application to the selected  
container without the problems associated with paper  
labels.

In addition, the polymeric film substrate for the label  
25 will be selected so that it will expand or contract to  
the same degree as the container so that when ambient  
conditions change, the label will not pucker or blister.

The polymeric materials include clear, opaque or colored  
30 polypropylene, polyethylene, polyester, polystyrene,  
polycarbonate, vinyl, cellophane or compatibilized  
blends.

The term "film facestock" or "polymeric label substrate"  
35 as used herein should be taken for purposes of the  
present invention to refer to a material compatible in  
terms of rigidity, deformability or conformability,  
recyclability if a plastic container and expansion or

5 contraction characteristics with the plastic or glass  
container to be labeled. Similarly, the "activatable  
hydrophilic layer" previously mentioned has the  
properties of minimal tack when dry so labels can be  
unwound from a roll or separated from a stack and once  
10 activated with moisture, it will have the properties of  
wet tack, absorbtivity, drying, sufficient adhesion to  
the polymeric label substrate and affinity and adhesion  
to the container or labeling adhesive if used as an  
activating medium in the wet or dry form.

15 Activatable hydrophilic layers containing at least 30%  
animal glue can be wet or remoistened without adhesive  
for use on a glass, plastic or metal container or a water  
based adhesive can be used to activate and affix the  
20 polymeric label substrate with the activatable  
hydrophilic layer to the glass, plastic or metal  
container. For deformable containers, the hydrophilic  
layer activated into an adhesive is formulated to form a  
bond with the container and the polymeric film substrate  
25 such that when dry, the strength of the container wall-  
hydrophilic adhesive interface and the cohesive strength  
of the adhesive itself are all greater than the forces  
required for deformation of the label.

30 As used herein and in the appended claims, the term  
"hydrophilic" is used to describe materials or mixtures  
of materials which bind, pass or absorb water. The term  
"activatable hydrophilic layer" describes a hydrophilic  
layer that when binding, passing or absorbing water  
35 becomes activated and transforms into an adhesive layer  
with wet tack and affinity for the container to be  
labeled. The term activated as used herein describes the  
change in a dry pre-applied dry hydrophilic layer on a



5 label substrate to a wet adhesive layer when activated with an aqueous medium that will adhere to the container wall to be labeled, dry and set up with strong adhesion.

The preferred "activatable hydrophilic" materials of the present invention are based on animal glue coating which in broad terms is an organic colloid of protein derivation from collagen which is a protein constituent of hide materials and bones obtained using well know techniques widely used to provide many commercially available glues. Hide animal glue is preferred over bone animal glue because of superior physical properties and strength. The animal source is not critical and glues may be derived from wild or domesticated animals such as horses, cattle, pigs, sheep and the like. Purified versions of animal glue are also known as gelatin. Animal glues are commonly graded on comparative gel gram strength values by manufacturers and provides a rough guide for use but this standard does not always measure their working qualities as adhesives for glass, plastic and metal containers. Considerations of gram strength, pH, ash content, clarity, grease content, type of glue (bone or hide), degree of purification and processing methods all have a bearing. The gram strength measurement of animal glue is also known as a gel strength measurement which ranges from about 30 grams (weak) to 500 grams (exceptionally strong) where the highest gram strengths contain greater amounts of reactive glue protein. Typically, stronger adhesive bonds are achieved with higher gram strength animal glues and blends of animal glues. Unfortunately, as gram strength increases, so does the dry brittleness of the glue which must be addressed in formulating using modifying components such

5 as plasticizers, humectants and modifying synthetic resin dispersions.

In physical form, dry animal glues are odorless, relatively tack free hard materials ranging in clarity  
10 from light amber to dark brown depending on the origin, processing technique and degree of purification that contain 10 - 14% moisture. Almost all grades can be made up into aqueous solutions and many can be melted and applied at temperatures less than the boiling point of  
15 water such as through a die or extruder as long as it is vented for potential moisture that could flash off. When aqueous formulations are prepared, the moisture content of the hard material is included in calculating the amount of water added to obtain the desired weight  
20 percent dispersion in water of the animal glue. For a clear polymeric substrate, clarity or contact clarity of a thin activatable hydrophilic layer comprising at least 30% animal glue by dry weight dictates that relatively clear and pure animal glue is preferably used.

25 In water, solutions of animal glues based on hide which are typically the higher gram strength variety preferred for use in this invention instead of bone based glues are generally reaction neutral and have a pH range of 6.4 -  
30 7.4 which is a pH that makes them compatible with many other materials. The specific gravity of dry animal glue is approximately 1.27.

An important feature of animal glue in the present  
35 invention is that when dry animal glue is placed in cold water like an ice chest for beverages, animal glues do not dissolve readily but swell absorbing considerable water forming a gel state and must be heated to dissolve

5 into solution at 100 - 140 °F. The rapid development of  
a gel state when wet with an aqueous medium provides a  
fast set and tackiness with quick development of initial  
bond and holding strength which is critical for the  
successful application of polymeric labels to glass,  
10 plastic and metal containers using wet labeling  
techniques. For applications where long term contact with  
water and subsequent swelling of the animal glue could  
cause a loss of adhesion, it is preferred to crosslink  
the animal glue to make it moisture resistant. One of the  
15 keys to this invention is maintaining the beneficial  
properties of non cross-linked animal glue for label  
application using at least 30% animal glue in the  
activatable hydrophilic layer which is then cross-linked  
and rendered moisture resistant after application by the  
20 water containing a cross-linker or adhesive containing a  
cross-linker which is applied when the hydrophilic layer  
is activated into an adhesive. High speed labelers run  
from 200 - 1,200 container per minute and the cross-  
linking reaction is relatively slow at even at high  
25 levels of cross-linker so the layer can be wet, develop  
tack and adhesion to the container to be labeled and cure  
to moisture resistant over time. This time period varies  
depending on the activatable layer formulation, cross-  
linker of choice and amount of each component used along  
30 with the amount of water that must be absorbed and dried.  
The time period can run from 12 hours to 14 days but  
stable formulations that are rendered moisture resistant  
in 72 hours are adequate for most commercial labeling  
applications. A key advantage of cross-linked activated  
35 adhesives consisting predominantly of animal glue is that  
when dry and rendered moisture resistant, the adhesive is  
not impervious and hard and in fact the adhesive layer  
will "give" or move slightly under high moisture

5 conditions and contact the surface to be labeled on  
drying providing a "live" adhesive bond that takes up the  
stresses and strains that normally occur under labeling  
and drying conditions. Another key benefit of an adhesive  
layer containing animal glue that forms a gel structure  
10 is that if the surface to be labeled is cool, the animal  
glue component will gel faster and set a bond faster  
because it is less fluid. This can be an important factor  
in brewery applications where post mold labeling of cold  
beer or cold storage of labeled containers can accelerate  
15 the bond of the activatable layer.

Another important feature of animal glue layers,  
particularly those deposited from water or wet with water  
is that when dry, they exhibit high adhesive strength,  
20 are continuous, non-crystallizing, non-cracking and of  
great strength and elasticity. Additionally, animal glue  
is reaction neutral, relatively odorless, non toxic and  
non corrosive. Due to its unique protein structure,  
animal glue is not precipitated by acids or alkali's and  
25 is resistant to structural breakdown by acids or alkali's  
within normal practical limits so for use as a labeling  
adhesive where the contents of a container could leak or  
drip down the side of the container and attack the  
adhesive, animal glue is durable. Animal glue based  
30 adhesives are also resistant to grease, oil, alcohol and  
other chemicals that are free of water and as stated  
above, to overcome moisture sensitivity, animal glue can  
be rendered moisture resistant by cross-linking.

35 For glass containers, it is preferred to use high gram  
strength animal glues at a level of at least 50% dry by  
weight of the activatable hydrophilic layer to achieve a

5 strong bond where the gram strength of the animal glue is greater than 50 grams and more preferably in the range of 175 - 225 grams. More preferably, for glass containers a dry level of animal glue between 60-80% is preferred as is a gram strength in excess of 175 grams (also known as  
10 gel strength). The higher the gel strength of the animal glue, the stronger the adhesive bond to glass will typically be but also the more brittle the bond will become, especially after crosslinking so the 175 - 225 gram range while not limiting, is preferred for many  
15 applications. Animal glue shows a specific affinity for glass and coated glass and is ideal as a base component to be formulated into an activatable hydrophilic adhesive layer because of its strong wet tack and affinity for glass. Animal glue has such a strong affinity for glass  
20 that some formulations when dry and adhered to the glass will pull glass particles with it when removed. This has been proven by those that use animal glue to create chipped glass or frosted glass decorative designs using animal glue allowed to dry on glass that is subsequently  
25 removed. This high affinity and bond strength to glass is why animal glue is the key component of this invention for activatable layers on polymeric films for high speed post mold labeling.

30 For plastic containers, it is recommended to blend synthetic acrylic polymers which bind or absorb water and become adhesives such as polyacrylic acid, polyacrylic acid copolymer or carboxylated sodium polyacrylate with the animal glue to promote adhesion to the plastic  
35 container wall. For plastic containers, the dry animal glue level in the activatable layer can range from 30-80% but it is preferred at a level of 35-45% in combination with synthetic polymers. Moisture sensitive synthetic

5 polymers that can be rendered insoluble through cross-linking can be added at levels up to 70% dry polymer

Amounts of non moisture sensitive synthetic polymers can also be added as modifiers at levels up to 50% dry  
10 polymer but most preferably at levels up to 25% dry polymer.

If synthetic polymers are used, they can be in the form of solutions, dispersions and emulsions but solution polymers are preferred.

15 In addition to synthetic resins as discussed above, animal glue solutions are compatible with select natural resins, modifying additives such as plasticizers, oils, fats, waxes along with other adhesive materials such as  
20 casein, starch, dextrine and gums under certain conditions.

To plasticize and increase the flexibility of animal glue and control lay flat, humecants (plasticizers) such as  
25 urea, polyethylene glycol, glycerin, sorbitol, cane or invert sugars or combinations of the preceding are added at levels up to 40% dry and most preferably 25-30% dry depending on the properties desired but preferably at levels < 30% if the activatable layer is subsequently to  
30 be reacted (cross-linked) to be rendered resistant to moisture to minimize the level of non-reactive components in the matrix of the activatable hydrophilic layer. It is noted that urea acts as a gel dispersant to reduce the viscosity of the gel for coating applications while it is  
35 inert in the animal glue matrix.

As discussed above, a preferred aspect of the present invention is to use cross-linkable (reactive) components

5 in the activating aqueous solution to react with the hydrophilic layer that converts into an adhesive that cures to become more moisture resistant as it dries and builds adhesion to the container wall. Not only does the cross-linking agent make the activated adhesive more  
10 moisture resistant, it can provide greater initial wet tack versus using water only and promotes adhesion to the container wall while increasing chemical resistance to materials that may come in contact with the adhesive layer.

15 Examples of synthetic cross-linkable materials are those which contain carboxyl groups, hydroxyl groups or other functional group which will react with a cross-linking agent. The cross-linking agent can also be added to an  
20 adhesive used to wet and activate the hydrophilic layer. When water and a cross-linking agent are combined, the composition will comprise 0.005 -10% by wt. of cross-linking agent. Preferred crosslinking agents are Polycup 172 from Hercules and Glyoxal available from BASF  
25 Corporation.

The coated, extruded or coextruded activatable hydrophilic layer converts to a wet tacky adhesive layer when wet with an aqueous solution which is defined as a  
30 substance capable of combining two surfaces by the formation of a bond. If a light deposition of an aqueous adhesive is used as the activating medium, the activatable hydrophilic layer bonds to the polymeric film substrate and the glass, metal or polymer of the  
35 container wall when dry.

The use of the properly formulated activatable hydrophilic layer for a given polymeric labeling substrate and container to be labeled will have a direct

5 effect on the speed which the labeling line can be run.  
When considering the choice of the activatable material  
which forms the hydrophilic layer, which may be applied  
by coating, coextrusion or extrusion, one must consider  
the label substrate, container to be labeled, labeling  
10 machinery, activation technique and down stream  
processing requirements such as filling, conveying and  
packing. In addition the final appearance of the label  
such as the clear no label look or a plain opaque or  
metalized label must be considered in the choice of the  
15 components of the hydrophilic layer. Generally, a deposit  
of from 0.25 to 8 lbs./3000 square feet of the  
activatable hydrophilic layer, when dried, may be  
employed on the polymeric film layer, depending on the  
particular material that is selected and the method that  
20 is used to apply the layer such as coating, coextrusion  
or extrusion.

It is critical to the successful application and use of  
an activatable hydrophilic polymeric film label to  
25 control how the water or water based adhesive is applied  
to the activatable hydrophilic layer, how deposition  
(weight or thickness) is controlled and how the resultant  
combination with the container is pressed together.  
Generally, from <0.05 to 2.5 g. /sq. ft. of activating  
30 medium (water or water based adhesive) is applied to the  
pre-applied activatable hydrophilic layer with 100%  
coverage of the label with a preferred range of 0.1-0.25  
g. / sq. ft. If a grid or other pattern of activating  
medium is employed, then the amount of activating medium  
35 may be reduced. If a grid pattern is employed, the  
hydrophilic layer may be applied to be substantially in  
register with the activating medium.



5 It is critical to the successful application and use of  
an activatable hydrophilic polymeric film label to  
precisely control how the amount of aqueous activating  
fluid medium (water, water plus a cross-linker, adhesive  
or adhesive plus a cross linker) is applied. To much  
10 aqueous medium for a given deposition of activatable  
hydrophilic layer will overpower the layer and will  
result in loss of tack and initial adhesion and will  
result in labels 'swimming: or moving as the labeled  
container is conveyed, filled or packed and will increase  
15 the drying time of the activated layer to produce a firm  
adhesive bond to the wall of the labeled container. Not  
enough aqueous activating medium will not completely  
develop the full adhesive properties of the activatable  
layer and will result in poor bonds.  
20 For optimum aqueous medium application control, optical  
appearance and uniformity, it has been found that it is  
preferable to use smooth applicator pallets to apply the  
activating solution which for purposes of this invention  
includes water, water plus a crosslinking agent, adhesive  
25 or adhesive plus a crosslinking agent. The activating  
solution is not limited to these components but will  
include them as a major portion of the activating  
solution with minor components such as biocides, wetting  
agents, fragrances, humectants, defoaming agents,  
30 viscosity modifiers and rheological modifiers also  
contemplated.

In a preferred embodiment, conventional hard rubber,  
metal or aluminum glue applicator pallets are modified by  
35 adhering a compressible surface like a foam layer with a  
smooth surface to the adhesive or activating side of the  
pallet. This allows for intimate contact between the  
applicator pallet and applicator metering roll when the

5 activating solution is applied to the compressible surface and for intimate contact between the wetted pallet and the hydrophilic layer when the wetted pallet with activating solution is pressed in intimate contact with the hydrophilic layer. Compression of the soft foam  
10 like layer as it contacts the wetted applicator roll in contact with the activating solution is important as a means of uniformly controlling pick up of the activator solution. As detailed earlier, it is critical to control the deposition of the activating medium to a low level.

15 The compression of the foam modified pallet in combination with the gap adjustment of the applicator roll system allows for uniform metering and control of the activating solution. An added benefit is that the compression causes a wiping action as the compressible  
20 surface of the applicator pallet rotates past the applicator roll to pick up the activating solution providing for a uniform application of solution where uneven application or even foam is smoothed out and made uniform.

25 When the wetted compressible pallet comes in contact with the activatable hydrophilic layer to pull the label out of the basket for application, the compressible pallet applies pressure on the hydrophilic layer and provides  
30 for uniform application and wetting of the activatable hydrophilic layer to promote best optical clarity and ultimate adhesion of the label after drying.

The modified compressible surface must be smooth and  
35 wettable which means the activating solution must wet out on the surface. In a preferred embodiment, the foam will compress at least 5% of its thickness for the optimum wiping action and will have a durometer of < 50. More

5 preferred is a compressability of about 5-50% of the  
thickness of the foam of the applicator and preferably  
>10% and a durometer of about 10-40 and preferably < 30  
with a glass smooth surface. The type of compressible  
foam like substance is not limiting but durable compounds  
10 like silicone and urethane polymers are preferred.

As with any adhesive labeling technique, the type of bond  
achieved is a fine balance between the container surface  
to be labeled, the label material, adhesive formulation  
15 which in this case is the activatable hydrophilic layer  
in combination with the aqueous activating fluid and the  
deposition of the activated adhesive. For purposes of  
this invention, the adhesive layer is the combination of  
the activatable hydrophilic formulation and the  
20 activating medium whether it is water, water and a cross-  
linking agent, adhesive or adhesive and a cross-linking  
agent. The ultimate adhesion properties are controlled by  
the surface characteristics of the material to be labeled  
and the choice of adhesive layer formulation and  
25 deposition of the adhesive layer

When using an adhesive or adhesive and cross-linker as  
the activating fluid, it will generally be possible to  
reduce the typical amount of adhesive applied to the  
30 activatable hydrophilic layer of the label to an amount  
which is <40% of the amount that is typically employed  
for affixing paper labels to a surface and preferably  
less than 20%. For example from 0.02 g. to 0.7 g. /sq.  
cm. may be used for the preparation of labels  
35 manufactured from polymeric films with a thickness range  
from 1.5 to 8 mils.

5 The choice of the adhesive layer made up of the  
activatable hydrophilic layer and activating medium, the  
type of label substrate and container to be adhered  
together, the plant processing conditions after labeling,  
storage requirements and the end use requirements that  
10 must be met such as high temperature resistance, ice  
proofness or passing a 24 - 72 hour ice bath soak are  
important considerations. There are many more specific  
variables within these considerations all of which  
influence the formulation of the proper activatable  
15 hydrophilic layer and activating medium for a specific  
application.

The bonding of the activatable layer can be accomplished  
with mechanical (non smooth surfaces) and specific  
20 adhesion. It has been found that the preferred animal  
glue component of the activatable layer provides superior  
adhesion characteristics when the layer is activated by  
water or a water based adhesive containing a cross-  
linking agent or a combination of cross-linking agents  
25 such as zirconium salts of mineral acids, such as Bacote  
20 from Magnesium Elektron, Inc., water soluble  
polyamide-epichlorohydrin material such as Polycup 172  
from Hercules, Glyoxal available from BASF Corporation or  
an aldehyde donor such as Glutaraldehyde that rapidly  
30 cross-links the animal glue and the like which may be  
used at a level of 0.01-8% by weight of the activatable  
layer composition.

Mechanical adhesion is defined as the bonding between  
surfaces in which the adhesive holds the parts together  
35 by inter-locking action and actual physical penetration.  
Specific adhesion is the bonding between surfaces which  
are held together by molecular forces wherein the  
surfaces are non porous and no penetration is possible.

5 These forces are related to the polarity and size of the molecules, pore size of non smooth surfaces and the initial action in obtaining a bond when the activated surface is wet, becomes tacky and a bond develops through molecular forces.

10

In mechanical as well as specific adhesion, the activated hydrophilic layer must "wet" both surfaces completely or weak bonded areas will develop as it dries or "sets" resulting in a poor bond. Not only is wetting of the surfaces critical, penetration is also important and this is why a polymeric film that is cavitated, voided or porous on the activatable side is a preferred embodiment of the invention in combination with the activatable hydrophilic layer which is penetrated to a degree by the aqueous activating medium. Penetration is important since most combinations of surfaces to be adhered together involve at least one porous or absorptive surface which controls the "setting" characteristics. The preferred low density polymeric labels are made of polypropylene which is commercially available. The preferred density is 0.45 to 0.85; an especially preferred density is 0.50 to 0.65, as distinguished from the conventional polypropylene label stock which has a density above 0.9. These materials are sometimes referred to as cavitated, micro voided or foamed polypropylene. Other polymers which may be used include polyethylene, polyester, polystyrene, cellophane, polycarbonate or compatibilized polymer blends. It is preferred to utilize a low density polymeric label substrate in conjunction with a hydrophilic material such as the activatable hydrophilic layer on the polymeric label to allow for more rapid escape of water from the activating medium that is placed on the activatable hydrophilic layer on the back or

5 adhesive side of the low density polymeric label. One  
common technique to create cavitation or voids in a  
stretched polymeric film is to use incompatible particles  
that separate and create a void or pore as the polymeric  
film is stretched. A common particle used for creating  
10 cavitation or pores is calcium carbonate and animal glues  
have a strong affinity and bond for calcium carbonate  
that is typically found in many voided polymeric film  
layers the activatable adhesive composition will be  
applied to so it will have superior adhesion.

15

For non porous polymeric film substrates, to facilitate  
wetting of the surface and penetration, the activatable  
hydrophilic layer and activating fluid that combine into  
the adhesive must wet out the surface of the container to  
20 be labeled. This is accomplished by applying the  
activating medium to the selected activatable hydrophilic  
layer which when applied to the container to be labeled  
brings the hydrophilic layer activated into an adhesive  
and container wall into intimate molecular contact. By  
25 using an aqueous fluid activating medium that wets and  
penetrates the hydrophilic layer as well as the container  
surface, a fluid region is created that flows to cover  
the surface as completely as possible. This is critical  
to the invention where even an apparently smooth surface  
30 in reality is composed of a random network of hills and  
valleys. When the activated hydrophilic layer is in the  
wet condition, it serves as a wetting bridge to promote  
adhesion. The more rapidly the activated hydrophilic  
layer can be applied (pressed in intimate contact with  
35 the surface to be labeled), the greater the fluid region  
will be before the activating medium is absorbed into the  
hydrophilic layer, the better the wetting at the adhesive  
interface will be resulting in stronger ultimate bonds

5 and improved optical clarity if a clear film is used.

As previously mentioned, various commercially available natural polymer based products at significantly reduced coat weight can be used as an additive to the animal glue  
10 or in the aqueous activating medium with activatable hydrophilic layers to provide good adhesion of polymeric film layers to a plastic or glass surface. These materials include starch based adhesives or casein based adhesives now predominantly used for glass applications  
15 since they do not bond well to plastic or metal. Synthetic polymer based materials that may be employed are commercially available and include EVA based materials which have free carboxyl groups, converted starch solutions, PVA based adhesives, synthetic resin  
20 dispersions for metal or plastic containers or blends of synthetic and starch and/or casein based products and the like. Acrylic and acrylic/methacrylic polymer dispersions may also be used as synthetic polymer additives. Optionally, if just water or water and a cross-linking  
25 agent are used as the activating medium, it is preferred to thicken the water or solution for better machining on the labeler that is designed to handle higher viscosity mediums such as conventional labeling adhesives by adding a thickening amount of a thickener. Many commercially  
30 available thickeners can be used but special mention is made of the Laponite family of synthetic thickeners from Southern Clay Products that form a gel structure of an aqueous solution at low addition levels that will not overpower the adhesive properties of the activated medium  
35 and will not interfere with the ultimate bond or moisture sensitivity of the dry adhesive at the low levels used to thicken the aqueous solution. Aluminum silicate or other well known natural or synthetic gums may also be added.

5 It is clear that one specific activatable hydrophilic layer may not fit all applications but it has been found that the activatable hydrophilic layers of the present invention can be tailored to particular applications based on the conditions and requirements for wet PML  
10 labeling of polymeric substrates but the activatable layer must contain at least 30% by weight of the dry activatable layer of animal glue that when activated (wet) by an activating fluid medium becomes sufficiently tacky to adhere a polymeric layer to a container through  
15 filling, conveying, processing or packing that will subsequently dry and provide good adhesion to the container. When working with natural and synthetic activatable layers that are obviously sensitive to moisture, it is important depending on the moisture  
20 sensitivity of the formulation to add a humectant to the activatable layer at a level of 0.25-25% by dry weight to provide curl resistance and to impart lay flat properties to the polymeric film labels. The humectants also tend to act as plasticizing agents so the activatable layer does  
25 not become too brittle when dry and include urea, polyethylene glycols such as PEG400, polyvinyl alcohol, glycerin, sorbitol and the like.

For a coextruded product, if an adhesion promoting tie  
30 layer is employed, materials such as maleic anhydride, ethyl acrylic acid and the like may be employed at levels up to 5% by weight of the hydrophilic composition. For a coated product, if a primer is employed, materials such as chlorinated polypropylene, polyethylene imine (PEI),  
35 acrylic primers and the like may be employed at levels of 0.05-1.0 lbs/3000 sq. ft. Special mention is made of acrylic resin based primers that are filled with a silicate such as colloidal silica also known as "water



5 glass" that has demonstrated superior adhesion characteristics to animal glue that has a high natural affinity for glass and silicates such as alkali metal silicates.

10 Slip aids and anti-blocking compounds commonly used in the art can prevent excessive friction between the activatable hydrophilic layer and the printed label face and also control the effect of ambient moisture levels which may tend to cause label blocking and interfere with

15 the operation of high speed automated machinery which is used to apply labels. These materials may be used at a level of 0.05-5% by weight of the activatable layer composition and/or the protective over coat applied over the printed indicia on the side of the label opposite the

20 activatable layer and include materials such as microcrystalline wax emulsions, erucamide dispersions, polytetrafluoroethylene compositions, silicone beads, modified silicone solutions, parafin wax emulsions, high melting polypropylene emulsions, carnauba wax emulsions,

25 oxidized ethylene/EVA compositions, micronized polyethylene wax/PTFE emulsions, micronized polypropylene, micronized fluorocarbons such as PTFE (Teflon), micronized polyethylene, silica and talc. Specific mention is made of the use of silanes to

30 partially crosslink the animal glue in the coating matrix effectively reducing the surface moisture sensitivity of the coating to help prevent blocking and to create a more crystalline surface for improved slip. Of specific note are the Gransil series of silane crosslinkers available

35 from Grant Chemical, Paterson NJ and specifically Gransil 51 which is a  $\gamma$ -glycidoxypyrpyl-trimethoxy silane. A preferred defoamer is polypropylene glycol having a weight average molecular weight of about 200-600.

5 The wetting agent may comprise a non-ionic surfactant  
such as an ethoxylated nonyl phenol or an ethoxylated  
amine such as surfynol from Air Products & Chemicals  
Corporation.  
It is contemplated that the activatable hydrophilic layer  
10 can be applied in multiple coating steps to have a base  
layer with humectants for curl control that is very  
reactive to moisture and would tend to block with an  
overcoat of a less moisture sensitive layer that can be  
crosslinked that will resist blocking where the base  
15 layer will comprise from 50-90% of the total layer coat  
weight.

Protective coatings may be used to protect the exposed  
polymer film and printed indicia of the label when  
20 applied at a level of 0.25-4 lbs./3000 sq. ft. using  
conventional application techniques. These materials  
include styrenated acrylics such as OC1043 from O.C.  
Adhesives Inc., urethanes such as AS455 from Adhesion  
Systems Inc., Flexcon Release Varnish from Flint Ink. In  
25 a preferred embodiment, a protective coating with release  
(non stick) characteristics commonly known in the art is  
preferred as the protective overcoat to prevent blocking  
if the stacks of labels are exposed to moisture.

30 If an antistatic agent is employed in the printable over  
coat applied over the indicia, it may be present at a  
level of 0.5-3% by weight of the dry coating. These  
materials include quaternary ammonium salts such as  
Ethaquad C12, sulfonated styrene maleic anhydride,  
35 sulfonated polystyrene, sulfonated vinyl toluene maleic  
anhydride, conductive polymers and organo modified  
silicones such as Silwet L77. It is noted that anti-  
static agents are typically not needed in the activatable

5 layer because the high moisture content of the animal glue provides exceptional static elimination properties.

Optionally, if a metalized coating of a thin metal film is deposited on the polymeric sheets or rolls, premium  
10 quality decorative labels with all of the advantages set forth above will be provided.

It is clear that one specific activatable hydrophilic layer may not fit all applications but hydrophilic layers  
15 can be tailored to particular applications based on the conditions and requirements for wet PML labeling of polymeric substrates.

If an adhesion promoting tie layer or primer is employed  
20 to promote hydrophilic layer adhesion or adhesive adhesion, materials such as maleic anhydride, ethyl acrylic acid, carboxylated polyurethane resin and the like may be employed at levels of 0.1-3 lb/3,000 sq. ft.

25 If a cross-linking catalyst is added to the adhesion promoting tie layer, the ratio of catalyst to adhesion promoting tie layer may be an amount that is sufficient to cure the adhesion promoting tie layer. An excess of the catalyst, i.e. 5-25% in excess of the amount of the  
30 catalyst that is required to cure the adhesion promoting tie layer may be used to provide a portion of the catalyst at the interface of the adhesion tie promoter and the hydrophilic layer to increase the moisture resistance of the hydrophilic layer without decreasing  
35 the moisture absorbtivity of the hydrophilic layer. Additionally, excess catalyst can also be available to aid in curing of the adhesive.

- 5 The following formula may be utilized for preparing a layer which, after drying, may be utilized as label stock when treated with a suitable activating solution.

ACTIVATABLE HYDROPHILIC LAYER FORMING SOLUTION

- 10 Animal Glue 30-95wt% preferably 45-60wt%  
Synthetic Or Natural Polymers 5 - 65wt%, preferably 40-55wt%  
Cross-linker 0-5wt%, preferably , <2wt%  
Humectants 0-15wt%, preferably 5-10wt%
- 15 Wetting Agent 0-1wt%, preferably <0.5wt%  
Defoamer 0-1wt% preferably <0.5wt%  
Anti-block Additives 0-2wt %, preferably <1wt%  
Slip Additives 0-2wt %, preferably <1wt%  
Water balance to 100wt%
- 20 As noted above, different lots of animal glue in the "dry" state have different levels of retained moisture so that each batch will vary in the content of added water due to the varying water content of the different lots of
- 25 animal glue.

- When a glass substrate is to be labeled, higher levels of animal glue are generally required. When a plastic surface is to be labeled, higher concentrations of added
- 30 synthetic polymers are generally required.

The following describes an activating solution which may be used in the practice of the invention:

- 35 ACTIVATING SOLUTION

- Cross-linker 0-10wt%, preferably 1-10wt%; especially preferably, 2-4wt%  
Wetting Agent 0-1wt%, preferably <0.5wt%
- 40 Defoamer 0-1wt% preferably <0.5wt%  
Thickener 0-2wt%, preferably <1wt%  
Natural Polymers 0-15wt%, preferably 5-10wt%  
Synthetic Polymers 0-10wt%, preferably <5wt%

## 5 Water balance to 100%

The following examples illustrate the invention.

Defined terms and tests are as follows:

10

Wet Tack, - this is a measure of the initial adhesion of the label to a surface immediately after activation and application to the surface and evaluated by trying to push or slide the label on the surface it was applied to.

15

Ice Soak - Submersion of the labeled sample in an ice water/cold water bath at a temperature of about 33-38° for 72 hours. After 72 hours, the labeled article is rotated in the bath and labels are evaluated for edge flagging or  
20 removal.

Edge Difficulty - this is a measure of the degree of difficulty to lift the edge of the sample after it has been allowed to dry and cure for a specified time period.

25

W denotes wet test after ice soak, D denotes dry test.

Adhesion Rating - this is a measure of the degree of bond of the label to the surface when it is peeled back in a slow continuous motion by hand and is performed right  
30 after the edge difficulty test. If an ice soak test is performed, this test is performed on sample pre and post ice soak test.

35

Adhesive Action - defines whether the activatable layer splits, stays with the label or transfers to the labeled surface after the label is peeled back for the adhesion rating test. If an ice soak test is performed, this test is performed on sample pre and post ice soak test.

5

Curl - curl is defined as the degree the edges of the label specimen lift when exposed to changing environmental conditions in terms of temperature and humidity.

10

Blocking - is defined as the degree of tack versus separation of individual labels when the coated side of the label is in contact with the opposite side in a constant humidity chamber (92% RH) for 24 hours at room temperature. Since different films are used, for comparative test purposes the non adhesive side was always evaluated against the same Flexcon varnish from Flint Ink.

15

20 All tests except Adhesive Action are rated on a scale of 0 to 3 where 0 is failure, 1 is poor, 2 is good and 3 is excellent. Adhesive Action is denoted as A for split, B stays on label, C transfers to substrate to be labeled.

25

The term Sample Formulation describes the formulation of the activatable layer. The particular source of the animal glue is not critical and the key property of adhesion is specified as "gram strength". Materials denoted ACW are moisture absorbing acrylic polymers available from Noveon.

30

35 Approximate Coat Weight - is the theoretical coat weight based on the solids of the coating and draw down rod size in grams/ MSI MSI = 1000 sq.in. To convert to metric

5 equivalent, multiply grams / MSI x 1.55 for grams / sq.  
meter

Type Of Film Used - PET denotes clear polyester - 2  
mil Shimpex

10

OPP denotes 2 mil clear oriented  
polypropylene 196LL from  
ExxonMobil or TL50 from Inteplast

15

WOPP denotes 3.4 mil white cavitated  
oriented polypropylene 85LP from  
ExxonMobil

20

OPS denotes 2 mil oriented polystyrene  
from Alcoa Kama

All films were corona or flame treated to enhance  
adhesion. Corona treatment is a process which utilizes a  
voltage source, an electrode, a dielectric and a ground.  
25 High voltage is applied to the electrode and the  
dielectric is placed between the electrode and the  
ground. The dielectric comprises the substrate, an  
insulator, such as a silicone or a ceramic and air. The  
voltage buildup on the electrode ionizes the air in the  
30 electrode/substrate gap, causing the formation of highly  
energized corona which excites the air molecules,  
reforming them into a variety of free radicals which then  
bombard the substrate surface increasing its polarity by  
distributing free bond sites across it. The treater may  
35 use a dielectric covered roll or a bare-roll which uses a  
dielectric covered electrode. a system for corona  
discharge treatment may comprise a modified corona  
treater such as Model AB1977 using a power supply Model

- 5 No. AB6628, both of which are available from Pillar Technologies, Inc., Heartland WI.

Surface Labeled - G denotes glass, PET denotes polyester, HDPE denotes High Density Polyethylene

10

The technique to prepare samples is as follows:

- 1 - Prepare Activatable Hydrophilic formulation
- 15 2 - Draw down Activatable formulation on selected film substrate
- 3 - Dry in forced hot air oven
- 4 - Prepare Activator Solution
- 5 - Apply Activator Solution with foam pad or brush to
- 20 activate with the minimum amount of solution to activate the coating
- 6 - Rapidly apply the activated label to the surface to be labeled
- 7 - Allow the applied label to dry/cure for 7 days.

25

All coating and activator formulations are specified in parts by weight per 100 parts of composition and refer to dry parts of components except water.



5

## Example 1

10 Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue  
                   5 parts Urea  
                   5 parts Glycerine  
                   60 parts water

15 Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 1 part Polycup 172  
                           1 part Glyoxal  
                           98 parts water

20

Substrate To Be Labeled - G

25      Wet Edge Difficulty      Adhesion Rating      Adhesive Action  
       Tack    Pre/Post Ice Soak    Pre/Post Ice Soak    Pre/Post Ice  
       Soak

          3                    3\* / 2                    3 / 2                    A / A

30      \* - film begins to destruct

Curl Blocking    Ice Soak

3+            2                    3

35

## Example 2

40 Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue  
                   5 parts Urea  
                   5 parts Glycerine  
                   59.8 parts water

45

0.2 parts Silane Crosslinker Gransil 51

Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

50      Activator Formulation - 1 part Polycup 172  
                                   1 part Glyoxal  
                                   98 parts water

Substrate To Be Labeled - G

55

5

Wet Edge Difficulty Adhesion Rating Adhesive Action  
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
Soak

10 3 2 / 2+ 3 / 3 A / A

Curl Blocking Ice Soak

15 2 3 3

### Example 3

20

Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue

5 parts Urea

5 parts Glycerine

25

59.8 parts water

0.2 parts Silane Crosslinker Gransil 51

Film Type - OPP

Approx. Coat Weight - 4.5 grams/MSI

30

Activator Formulation - 1 part Polycup 172

1 part Glyoxal

98 parts water

35

Substrate To Be Labeled - G

Wet Edge Difficulty Adhesion Rating Adhesive Action

Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice

40

Soak

3 3 / 2 2+ / 1+ C / C

Curl Blocking Ice Soak

45

1+ 3 3

### Example 4

50

Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue

55

5 parts Urea

5                    5 parts Glycerine  
                      59.8 parts water  
                      0.2 parts Silane Crosslinker Gransil 51

Film Type - OPS  
 10    Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 1 part Polycup 172  
                              1 part Glyoxal  
 15                         98 parts water

Substrate To Be Labeled - G

20    Wet Edge Difficulty Adhesion Rating Adhesive Action  
       Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
       Soak  
       3                    3 / 2\*                    2+ / 2                    A / C

25    \* Film Splits

Curl Blocking Ice Soak

3                    3                    3  
 30

#### Example 5

35    Activatable Hydrophilic  
       Formulation - 30 parts 192 gram strength Animal Glue  
                          2.5 parts Urea  
                          2.5 parts Glycerine  
 40                         64.9 parts water  
                          0.1 parts Silane Crosslinker Gransil 51

Film Type - OPP  
 45    Approx. Coat Weight - 3.2 grams/MSI

Activator Formulation - 1 parts Polycup 172  
                              1 parts Glyoxal  
                              98 parts water

50    Substrate To Be Labeled - G

Wet Edge Difficulty Adhesion Rating Adhesive Action  
 55    Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
       Soak

$$5 \quad 3 \quad 3+ / 3^* \quad 2 \quad A / A$$

\* - Film begins to randomly destruct

## Curl Blocking Ice Soak

10

3 2 3

### Example 6

15

## Activatable Hydrophilic

20 Formulation - 30 parts 192 gram strength Animal Glue  
2.5 parts Urea  
2.5 parts Glycerine  
64.9 parts water  
0.1 parts Silane Crosslinker Gransil 51

25 Film Type - WOPP  
Approx. Coat Weight - 3.2 grams/MSI

Activator Formulation - 1 part Polycup 172  
1 part Glyoxal  
98 parts water

Substrate To Be Labeled - G

35	Wet Edge Difficulty		Adhesion Rating		Adhesive Action	
	Tack	Pre/Post Ice Soak	Pre/Post Ice Soak	Pre/Post Ice Soak	Pre/Post Ice Soak	Pre/Post Ice Soak
	3+	3 / 2	2+	/ 2		C / C

40 Curl Blocking Ice Soak

$$2+ \quad 2 \quad \cdot \quad 3$$

### Example 7

45

Activatable Hydrophilic

50      Formulation -    30 parts 192 gram strength Animal Glue  
                             5 parts Urea  
                             5 parts Glycerine  
                             60 parts water

Film Type - PET  
Approx. Coat Weight - 2.5 grams/MSI

55

- 5 Activator Formulation - 1 part Polycup 172  
1 part Glyoxal  
98 parts water

Substrate To Be Labeled - G

- 10 Wet Edge Difficulty Adhesion Rating Adhesive Action  
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
Soak

- 15 3 3 / 2 2.5 / 1.5 A / C

Curl Blocking Ice Soak

- 20 3 2 3

#### Example 8

- 25 Activatable Hydrophilic  
Formulation - 30 parts 192 gram strength Animal Glue  
5 parts Urea  
5 parts Glycerine  
30 60 parts water

Film Type - PET  
Approx. Coat Weight - 7.2 grams/MSI

- 35 Activator Formulation - 1 part Polycup 172  
1 part Glyoxal  
98 parts water

Substrate To Be Labeled - G

- 40 Wet Edge Difficulty Adhesion Rating Adhesive Action  
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
Soak

- 45 3 3 / 3 3 / 3 A / A

Curl Blocking Ice Soak

- 2+ 1 3

- 50 Example 9

- 55 Activatable Hydrophilic  
Formulation - 30 parts 192 gram strength Animal Glue

5                   5 parts Urea  
                   5 parts Glycerine  
                   59.8 parts water  
                   0.2 Silane Crosslinker Gransil 51

Film Type - PET

10   Approx. Coat Weight - 7.2 grams/MSI

Activator Formulation - 1 part Polycup 172  
                           1 part Glyoxal  
                           98 parts water

15   Substrate To Be Labeled - G

Wet Edge Difficulty Adhesion Rating Adhesive Action  
 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
 20   Soak

3               3 / 3 \*                   3 / 3                   A / A  
 \* - Film Destroys

25   Curl Blocking Ice Soak

1               3               3

Example 10

30

Activatable Hydrophilic  
 Formulation - 30 parts 192 gram strength Animal Glue

35               2.5 parts Urea  
                   2.5 parts Glycerine  
                   64.9 parts water  
                   0.1 parts Silane Crosslinker Gransil 51

40   Film Type - OPP  
 Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 1 part Polycup 172  
                           1 part Glyoxal  
 45                       88 parts water  
                           10 parts sucrose

Substrate To Be Labeled - G

50

Wet Edge Difficulty Adhesion Rating Adhesive Action  
 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice Soak

55   3               3+ 3                   3 / 2                   C / C

5

<u>Curl Blocking</u>	<u>Ice Soak</u>
3	2
	3

## Example 11

10

## Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue  
 2.5 parts Urea  
 2.5 parts Glycerine  
 64.9 parts water  
 0.1 parts Silane Crosslinker Gransil 51

20

Film Type - OPP

Approx. Coat Weight - 2.2 grams/MSI

Activator Formulation - 1 part Polycup 172

25

1 part Glyoxal

88 parts water

10 parts sucrose

Substrate To Be Labeled - G

30

Wet Edge Difficulty Adhesion Rating adhesive Action.

<u>Tack</u>	<u>Pre/Post Ice Soak</u>	<u>Pre/Post Ice Soak</u>	<u>Pre/Post Ice Soak</u>
Soak			

35

2

2+ 1+

2 / 1+

C / C

<u>Curl Blocking</u>	<u>Ice Soak</u>
3	2+
	3

## Example 12

40

## Activatable Hydrophilic

Formulation - 30 parts 150 gram strength Animal Glue  
 5 parts Urea  
 5 parts Glycerine  
 60 parts water

Film Type - OPP

50

Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 2 part Polycup 172

55

2 part Glyoxal

96 parts water

5

Substrate To Be Labeled - G

Wet Edge Difficulty Adhesion Rating Adhesive Action  
 10 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
Soak  
 3+ 3 / 2+ 2+ / 2 C / C

15 Curl Blocking Ice Soak  
 3 2 2+

Example 13

20

Activatable Hydrophilic  
 Formulation - 30 parts 400 gram strength Animal Glue  
                   5 parts Urea  
                   5 parts Glycerine.  
 25                 60 parts water  
                   Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

30 Activator Formulation - 2 part Polycup 172  
                               2 part Glyoxal  
                               96 parts water

Substrate To Be Labeled - G

35

Wet Edge Difficulty Adhesion Rating Adhesive  
 Action  
 40 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
Soak  
 3+ 2+ / 2 2 / 2\* C / C  
 \* - Observed very crystalline and fractures easily

45 Curl Blocking Ice Soak  
 1+ 3 3

Example 14

50

Activatable Hydrophilic  
 Formulation - 30 parts 192 gram strength Animal Glue  
 55                 5 parts Polyethylene Glycol



5                                      65 parts water  
 Film Type - PET  
 Approx. Coat Weight - 4.5 grams/MSI

10                                      1 part Polycup 172  
    1 part Glyoxal  
    88 parts water  
    10 parts sucrose

Substrate To Be Labeled - G

15                                      Wet   Edge Difficulty   Adhesion Rating   Adhesive Action  
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
Soak

20                                      3                                      3 / 2                                      3 / 2                                      A / A

\* - film begins to destruct

25                                      Curl Blocking   Ice Soak

   3                                      3                                      3

   Example 15

30

   Activatable Hydrophilic

35                                      Formulation -   40 parts 192 gram strength Animal Glue  
                                         59.8 parts water  
                                         0.2 parts Polypropylene Glycol

Film Type - PET

40                                      Approx. Coat Weight - 4.5 grams/MSI

   Activator Formulation -   1 part   Polycup 172  
                                         1 part   Glyoxal  
                                         98 parts water

45                                      Substrate To Be Labeled - G

   Wet   Edge Difficulty   Adhesion Rating   Adhesive Action

50                                      Tack Pre/Post Ice Soak   Pre/Post Ice Soak   Pre/Post Ice

   3                                      3 / 2                                      3 / 2                                      A / A

\* - film begins to destruct

55

5

Curl Blocking Ice Soak

2            2            3

10

## Example 16

15

## Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue

5 parts Urea

5 parts Glycerine

20

60 parts water

Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

25

Activator Formulation - 5 parts Polycup 172

5 parts Glyoxal

90 parts water

Substrate To Be Labeled - G

30

Wet    Edge Difficulty    Adhesion Rating    Adhesive Action

Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
Soak

35

3            2 / 2            1+ / 1+            A / A

40

Curl Blocking Ice Soak

3            2            3

45

## Example 17

50

## Activatable Hydrophilic

Formulation - 35 parts 400 gram strength Animal Glue

2.5 parts Urea

2.5 parts Glycerine

60 parts water

55

Film Type - PP

5

Approx. Coat Weight - 2.5 grams/MSI

Activator Formulation - 1 part Polycup 172  
 1 part Glyoxal  
 0.1 parts Gluteraldehyde  
 97.9 parts water

10

Substrate To Be Labeled - G

15

Wet Edge Difficulty Adhesion Rating Adhesive Action  
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
Soak

3 2 / 1+ 2 / 1+ C / C

20

\* - Observed very crystalline and fractures easily

Curl Blocking Ice Soak  
 3 2+ 3

25

Example 18

30

Activatable Hydrophilic  
 Formulation - 15 parts 400 gram strength Animal Glue  
 15 Parts ACW97-19 Acrylic Resin  
 70 parts water

35

Film Type - PET  
 Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 2 parts Polycup 172  
 2 parts Glyoxal  
 96 parts water

40

Substrate To Be Labeled - PET

45

Wet Edge Difficulty Adhesion Rating Adhesive Action  
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
Soak

50

3 2 / 1 1+ / 1 A / B

Curl Blocking Ice Soak

55

5 3 2 2

## Example 19

10

Activatable Hydrophilic

- 15 Formulation - 15 parts 400 gram strength Animal Glue  
 15 Parts ACW97-19 Acrylic Resin  
 70 parts water

Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

20

Activator Formulation - 2 parts Polycup 172  
 2 parts Glyoxal  
 96 parts water

- 25 Substrate To Be Labeled - HDPE

30 Wet Edge Difficulty Adhesion Rating Adhesive Action  
TackPre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice Soak  
 3 2 / 1 1+ / 1 B / B

35

Curl Blocking Ice Soak

3 2 2

40

## Example 20

45

Activatable Hydrophilic

Formulation - 10 parts 400 gram strength Animal Glue  
 20 Parts ACW97-20 Acrylic Resin  
 70 parts water

50

Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 2 parts Aziridine  
 98 parts water

55

5 Substrate To Be Labeled - PET

10 Wet Edge Difficulty Adhesion Rating Adhesive Action  
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice  
Soak

15 3 2+ / 1+ 2 / 1+ B/ A

Curl Blocking Ice Soak

20 3 2 2